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Geochemical controls on dispersion of U and Th in Quaternary deposits, stream water, and aquatic plants in an area with a granite pluton

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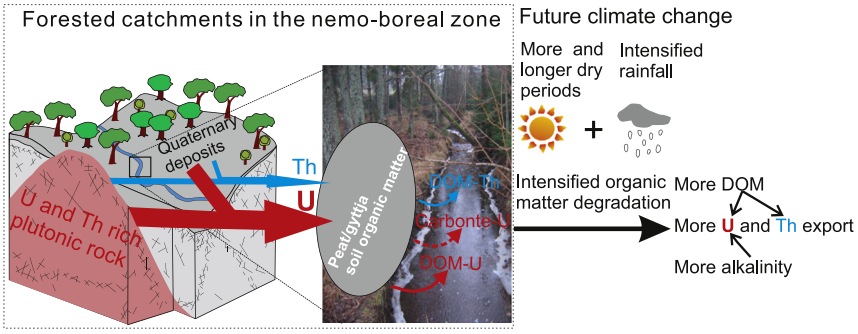
HIGHLIGHTS

- Granite plutons may be a source of U and Th to the environment.
- Sources and controls of U—Th in 4 nemo-boreal catchments were evaluated.
- Granite pluton and its erosional products were significant sources of U and Th.
- Organic matter and alkalinity were the key drivers for U and Th export.
- The export of U and Th may be enhanced by future climate change.

GRAPHICAL ABSTRACT



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ABSTRACT

The weathering of U and/or Th rich granite plutons, which occurs worldwide, may serve as a potentially important, but as yet poorly defined source for U and Th in (sub-)surface environments. Here, we assessed the impact of an outcrop of such granite (5 km in diameter) and its erosional products on the distribution of U and Th in four nemo-boreal catchments. The results showed that (i) the pluton was enriched in both U and Th; and (ii) secondary U and Th phases were accumulated by peat/gyttja and in other Quaternary deposits with high contents of organic matter. Movement of the ice sheet during the latest glaciation led to dispersal of U- and Th-rich materials eroded from the pluton, resulting in a progressive increase in dissolved U and Th concentrations, as well as U concentrations in aquatic plants with increasing proximity to the pluton. The accumulation of U in the aquatic plants growing upon the pluton (100–365 mg kg^{-1}, dry ash weight) shows that this rock represents a long-term risk for adjacent ecosystems. Dissolved pools of U and Th were correlated with those of dissolved organic matter (DOM) and were predicted to largely occur as organic complexes. This demonstrates the importance of DOM in the transport of U and Th in the catchments. Large fractions of $Ca_2UO_2(CO_3)_3^0(aq)$ were modeled to occur in the stream with highest pH and alkalinity and thus, explain the strongly elevated U concentrations and fluxes in this particular stream. In future climate scenarios, boreal catchments will experience intensified runoff and warmer temperature that favor the production of hydrologically accessible DOM and alkalinity. Therefore, the results obtained from this study have implications for predicting the distribution and transport of Th and U in boreal catchments, especially those associated with U and/or Th rich granite plutons.

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1. Introduction

The distribution, transport and environmental fate of U and Th in (sub-)surface environments are of environmental concern and have attracted growing attention (Abdelouas, 2006; Lidman et al., 2012; Maher et al., 2013; Köhler et al., 2014; Shin et al., 2016), primarily due to two reasons. First, U and Th are the only actinides that occur abundantly in natural environments, and thus can be used as natural analogues for the actinide series (Lidman et al., 2012). Second, U and Th are both chemically toxic and radioactive. The main pathways whereby U and Th enter aquatic environments include (i) weathering of rock and soil (Reimann et al., 2015); (ii) atmospheric deposition of terrigenous materials (Abdelouas, 2006) or industrial by-products, such as coal fly ash (Chen et al., 2018); and (iii) mining or processing of uranium ores (Abdelouas, 2006; Strok and Smodis, 2010; Momcilovic et al., 2013; Wang et al., 2017). Furthermore, the application of phosphate fertilizers can lead to an additional input of U into farmlands and associated waterbodies (Ahmed et al., 2014). Regarding rocks and soils, U and Th are typically enriched in igneous rocks of granitic composition that are formed during the final stage of a magma's crystallization and are widely distributed on all continents (Wilson and Åkerblom, 1980; Darnley, 1982; Khaleal et al., 2007; Dragović et al., 2014; Hwang et al., 2014; Shin et al., 2016). The release of U and Th from granite outcrops not only poses potential radiological and ecological threats to adjacent residents and ecosystems, but also may contribute significantly to the ultimate fluxes of U and Th to the global ocean. Yet, little research has been conducted to assess the impacts of U- and/or Th-rich granite outcrops and their erosional products on the distribution and transport of these actinides in the surface environment.

Uranium and Th released into the aquatic environment can be trapped by wetlands, in particular peatlands that are a common type of wetland containing an abundance of partially decomposed organic material (Owen and Otton, 1995; Porcelli et al., 1997; González A et al., 2006; Schöner et al., 2009; Lidman et al., 2012, 2013; Schumann et al., 2017). Peatlands occur widely in northern (boreal) Europe (Turunen et al., 2002), and thus play a controlling role in the cycling and mobility of U and Th in this region (Lidman et al., 2012, 2013). The peat is, however, frequently intermixed with Quaternary deposits such as till, clay/silt sediments and glaciofluvial material (Sohlenius and Hedenstroem, 2008). Therefore, these settings are likely to have an overall large and complex impact on mobility, transport, and redistribution of U and Th in the boreal landscape in particular.

In the aquatic environment, the speciation of U and Th varies widely as a function of pH, alkalinity, and availability of inorganic and organic ligands (e.g. CO_3^{2-}, PO_4^{-}, SO_4^{2-} and organic compounds). For example, the uranyl ion (UO_2^{2+}) complexed with SO_4^{2-} dominates at low pH (Bernhard et al., 1998), while under neutral to slightly alkaline conditions U is largely speciated as uranyl carbonate species (primarily $UO_2CO_3(aq)$, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) or calcium-uranyl carbonate ternary species ($Ca_2UO_2(CO_3)_3(aq)$ and $CaUO_2(CO_3)_3^{2-}$) depending on the availability of Ca (Bernhard et al., 1996; Shin et al., 2016; Tullborg et al., 2017). Although very little data is available for the aqueous speciation of Th under natural conditions, a few studies have shown that Th has a strong tendency to complex with sulfate and fluoride at low pH values, and with phosphate, hydroxide and carbonate under slightly acidic to alkaline conditions (Langmuir and Herman, 1980; Zhang et al., 2002). Furthermore, both of these two actinides have been predicted to be substantially complexed with dissolved (<0.45 μm) organic matter (DOM) in both experimental waters and boreal streams under mildly acidic and weakly alkaline conditions (Hongxia et al., 2006; Bouby et al., 2011; Lidman et al., 2012). Furthermore, as a strongly sorbing actinide, Th is highly reactive with mineral surfaces (Degueldre and Kline, 2007), and thus generally less mobile than U (Chabaux et al., 2003), and occurs in low concentrations in natural waters. For example, in 808 streams across Europe Th concentrations were overall very low (15–85th percentiles = 0.002–0.050 μg L^{-1}), however substantially elevated in streams draining the extensive forest and mire areas in northern Europe (15–85th percentiles = 0.016–0.120 μg L^{-1} for streams in Sweden-Finland, $n = 116$), where the concentrations of dissolved organic carbon (DOC), Fe and Al are also strongly elevated (Salminen et al., 2005). This points to an enhanced transport of Th by colloidal particles in north-European streams, supported by: (i) previous size-fractionated ultrafiltration experiments (Porcelli et al., 1997; Pokrovsky et al., 2006; Vasyukova et al., 2010); and (ii) the fact that boreal catchments and associated streams/rivers carry abundant colloidal organic matter and Fe hydroxides (Åström et al., 2012; Neubauer et al., 2013; Köhler et al., 2014; Sundman et al., 2014; Hirst et al., 2017), and also Al hydroxides together with Al-NOM (natural organic matter) complexes (Hagvall et al., 2015) in line with abundant gibbsite-like phases modeled for podzolized soils and surface waters in boreal landscapes (Gustafsson et al., 2001; Cory et al., 2006, 2007; Sjöstedt et al., 2010; Köhler et al., 2014).

The overall aim of this study was to define the environmental impact of an outcropping anorogenic granite on the distribution of U and Th in a nemo-boreal landscape located just south of the boreal zone. Previous studies have shown that chemical equilibrium modeling predicted by the geochemical program Visual MINTEQ can provide reliable information on (i) the speciation of metals and their surface complexation with organic matter and inorganic minerals (e.g., ferrihydrite and gibbsite) under both natural and experimental conditions; and (ii) fractional amounts of colloidal and suspended particulate Fe and Al carried by surface waters (Sjöstedt et al., 2009, 2010; Thorslund et al., 2014). For this study, Visual MINTEQ was used to model colloidal fractions of Al and Fe, as well as their potential roles in the transport of U and Th.

2. Materials and methods

2.1. Site description

The Swedish Nuclear Fuel and Waste Management Company (SKB) has been conducting site investigations in the Laxemar area on the Baltic east coast of Sweden for many years. As part of the investigation program, a number of streams within the area have been continuously monitored and analyzed for different physio-chemical and hydrological variables. For this study, four streams draining forested watersheds of different hydro-geographic and topographic characteristics (e.g., catchment size, elevation, mean discharge) were selected (Table 1, Fig. 1). These streams have strong seasonal variations in water flow rate that usually peaks during the spring snowmelt event, after intense rainfall in the summer, and from late autumn to mid-winter. The streams of Kärrsvik, Kårevik, and Laxemar are perennial, whereas the Ekerum stream is intermittent and usually ceases to flow at several locations during the summer (Berger et al., 2016). The bedrock underlying the catchments of the four streams is dominated by 1.8 Ga old granites and quartz monzodiorites, and dioritoid to gabbro, belonging to the Trans-Scandinavian Igneous Belt (Wahlgren et al., 2004, 2008). In the northeastern part of the Kärrsvik catchment, a 1.45 Ga old granite pluton (referred to as "Götemar granite") (Friese et al., 2012) out crops (Fig. 1). Except for the upslope areas where bedrock is exposed, the surface of the catchments is covered by unconsolidated Quaternary deposits including glacial till (frequently of sandy nature), glaciofluvial sediments, glacial and postglacial fine-grained (clay/silt) sediments (containing varying amounts of organic matter), postglacial sand and gravel, and peat (Sohlenius and Hedenstroem, 2008; Berger et al., 2016). In the low-lying areas (valley) where the stream tributaries flow, the Quaternary deposits are thicker with a maximum thickness of several meters and the land-use is dominated by arable land in addition to mixed/coniferous forests (Rudmark et al., 2005; Sohlenius and Hedenstroem, 2008). These areas are also characterized by relatively well-developed histosols (peat) or Gleysols (Rudmark et al., 2005; Sohlenius and Hedenstroem, 2008). The mean annual precipitation in the study area is 600 mm.

Table 1
Catchment characteristics and hydro-chemical properties of the studied streams.

			Kärrsvik	Kårevik	Ekerum	Laxemar
Catchment characteristics	Area (km^2)[a]		27.2	2.06	2.83	41.0
	Elevation (min–max, m.a.s.l)[a]		2–50	1-25	1-31	1–63
	Land cover[a]	Coniferous-and mixed forest (%)[b]	88	86	84	86
		Deciduous forest (%)	1	0	0	1
		Wetland (%)[c]	4	1	0	2
		Agriculture land (%)	4	5	12	5
		Water surface (%)	0	6	0	1
		Remaining open land (%)	3	2	4	5
Stream hydrochemistry	Mean discharge ($m^3\ s^{-1}$)[a]		0.144	0.011	0.015	0.216
	pH		5.90–6.69	6.06–6.50	7.07–7.87	5.92–7.03
	Alkalinity (mg L^{-1})		5.00–30.9	8.41–17.9	35.6–93.4	3.71–49.1
	F concentrations (mg L^{-1})		0.81–3.28	0.89–1.09	0.83–1.76	0.41–0.81
	P concentrations (mg L^{-1})		0.03–0.06	0.01–0.03	0.02–0.07	0.02–0.06
	NO_3^- concentrations (mg L^{-1})		0.15–1.33	0.16–0.32	0.06–1.20	0.04–3.08
	U concentrations (μg L^{-1})		0.52–1.36	0.38–0.74	0.36–2.56	0.13–0.66
	Th concentrations (μg L^{-1})		0.21–0.43	0.16–0.27	0.09–0.30	0.05–0.36
	U/Th concentration ratios		1.97–3.15	2.24–3.52	3.81–17.0	1.24–3.50
	U fluxes (g km^{-2} $year^{-1}$)		129	40	198	62
	Th fluxes (g km^{-2} $year^{-1}$)		49	16	25	28

[a] Data from Brunberg et al. (2004).
[b] Including cut forest.
[c] Including wetlands in both forest and open land.

2.2. Sampling and analysis of Quaternary deposits

In October–November 2012 and February 2015, <1 m to 5 m thick profiles of Quaternary deposits were sampled from the upper reaches (5 profiles), upon the Götemar granite (6 profiles) and lower reaches (7 profiles) of the Kärrsvik stream catchment (Fig. 1). Samples from each profile were collected in the field based on the occurrence of different soil types (Berger et al., 2016). For simplicity, we merged them into

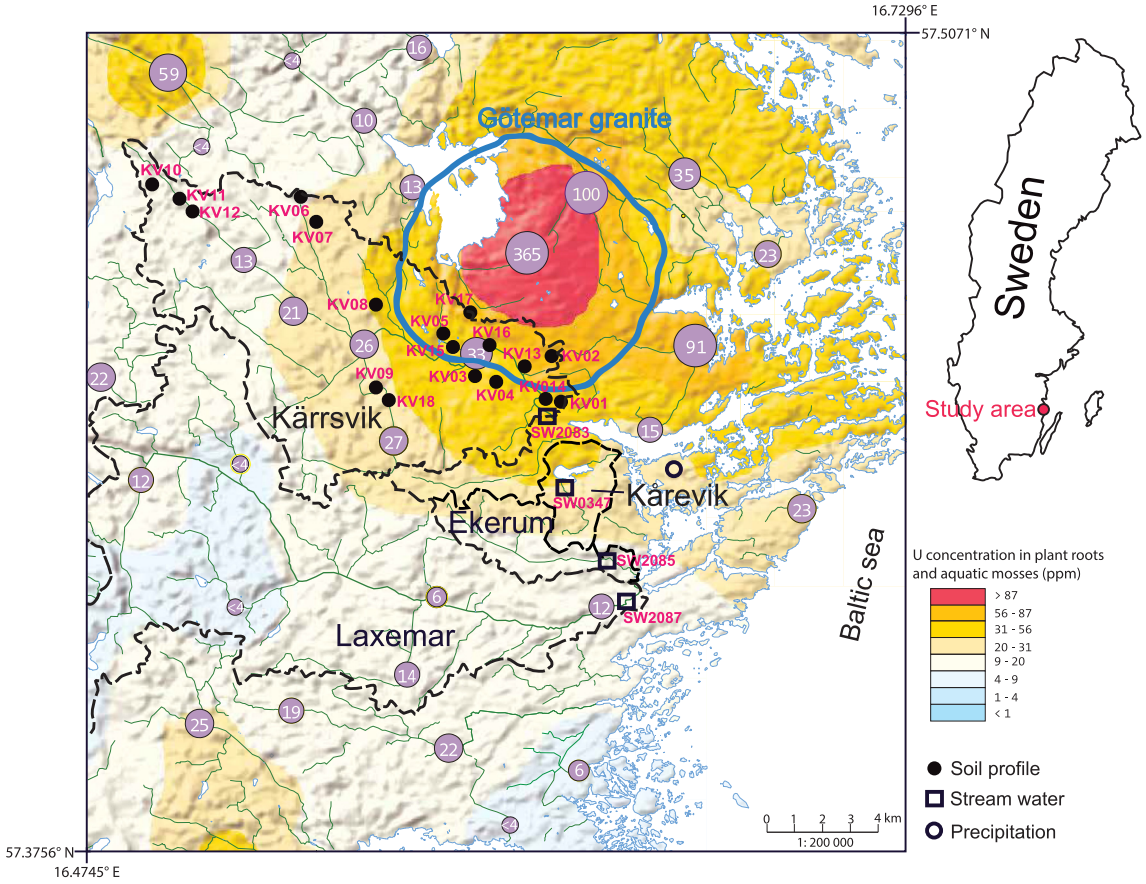

Fig. 1. The location of the investigated streams (Kärrsvik, Kårevik, Ekerum and Laxemar) and soil profiles ($n = 18$), precipitation sampling point, as well as the Götemar granite (dark blue circle). The growing symbols (values given within the symbols) refer to U concentrations in aquatic plant roots and mosses, whereas the color map is an interpolation of that data (U data and color-map were retrieved from the biogeochemistry database of the Geological Survey of Sweden).

five categories according to their organic matter concentrations and texture (e.g., grain size): (i) peat/gyttja, (ii) clay-gyttja/gyttja-clay, (iii) glacial clay or glacial/post-glacial clay-silt, (iv) fluvioglacial/postglacial sand and/or gravel, and (vi) till that was either gravelly sandy, clayey or silty. Each sample was dried at 60 °C, sieved through a 2-mm sieve and thoroughly mixed. Sample splits taken from four of the samples were separated into two size fractions (<63 μm and 63 μm to 2 mm), yielding a total number of 113 samples. The major physiochemical properties (e.g., pH, LOI, mineralogy) have been reported in previous work (Berger et al., 2016). All samples were pulverized and sent to Activation Laboratories Ltd., Ontario, Canada (ISO/IEC 17025 accredited) for analyses as described below.

In the lab, the pulverized samples were fused with lithium metaborate and lithium tetraborate in an induction furnace. The fuseate was then dissolved in diluted nitric acid. This method is presumed to efficiently attack both major oxides (e.g., quartz) and refractory minerals (e.g., zircon, sphene, monazite, chromite and gahnite), thus allowing a "near total" analysis of the elements in the samples. To evaluate the chemical partitioning of U and Th, a sequential chemical extraction (SCE) analysis was carried out as follows. The first SCE step involves the removal of water-soluble and exchangeable and calcite-bound species by shaking the sample with 1 M sodium acetate (NaAc) at pH 5 for 2 h at room temperature (Tessier et al., 1979). Next, the residue remaining after the first step was washed with deionized water and reacted at room temperature with an 8.9% sodium pyrophosphate (NaPp) solution (pH 9.5–10.5) for 1 h, to dissolve labile organic material including humic and fulvic acids (Hall et al., 1996; Hall, 1998). This reagent can, however, to some extent release inorganic Fe due to peptisation and dispersion of finely divided ferruginous particles (Hall, 1998). Finally, the remaining residue was washed with deionized water and extracted with an 8.2% hydroxylamine hydrochloride (HaHc) solution (pH < 2) for 2 h at 60 °C that will dissolve amorphous and crystalline Fe and Mn oxides (Hall, 1998) and acid-soluble (e.g., Al oxyhydroxides) phases (Åström et al., 2012). Included in the SCE analysis were 23 samples, including 15 2-mm sieved samples plus the <60 μm and 60 μm–2 mm fractions obtained from four of the samples (one gyttja and three till). Additionally, 15 2-mm sieved samples were extracted sequentially with only NaAc and HaHc.

The concentrations of U and Th in all resulting solutions were determined with an inductively coupled plasma mass spectrometer (ICP-MS). Analyses of blanks were carried out to measure background, duplicates to monitor analytical precision, and reference materials (GXR-1 and GXR-4, respectively) to determine accuracy and precision. The calculated analytical precision was <11%, while the accuracy was within ±9%.

2.3. Stream water and precipitation

From the SICADA database that is owned, quality-checked and managed by SKB, physio-chemical and hydrological data for two types of waters were retrieved in November 2017 (Sicada _17_102): (i) stream waters collected near the outlet of the four streams; and (ii) precipitation (rain and snow) from an open field east of the catchments (Fig. 1). The sampling and analytical methods used by the SKB geochemists and our criteria for selecting stream- water samples are given below.

2.3.1. Selection of stream waters

A water sample was included if the following criteria were fulfilled: (i) there were analytical results for pH, alkalinity, and the concentrations of DOC, U, Th and other major ions (Ca^{2+}, K^+, Na^+, Mg^{2+}, Sr^{2+}, Al^{3+}, Cl^-, F^-, PO_4^-, and SO_4^{2-}), and (ii) the charge balances were within ±5%. As a result, a total of 82 stream-water samples were included in the final dataset, encompassing approximately 4 years for Kärrsvik stream (December 2005–December 2009), 4 years for Kårevik stream (March 2006–December 2009), 6.5 years for Ekerum stream (June 2003–December 2009), and 12 years for Laxemar stream (December 2005–June 2017).

2.3.2. Sampling and analytical methods

The sampling procedures for the stream waters and subsequent analytical methods including uncertainties have been described elsewhere (Rönnback et al., 2008; Berger et al., 2012, 2015). To summarize, stream water was filtered through a 0.45 μm disposable filters and collected in 250 mL polypropylene bottles for measurements of pH, alkalinity, anions and DOC. In addition, filtered stream water was acidified with ultrapure HNO_3 and stored in 125 mL acid-washed polypropylene bottles for analyses of cations and trace elements. The pH values were determined with a potentiometer, and the alkalinity via acid-base titration within 24 h after sampling. The concentrations of Cl^-, F^- and SO_4^{2-} were determined by ion chromatograph (Methrom IC, 882), and DOC by a carbon analyzer (Shimadzu TOC 5000). The concentrations of Na, K, Ca, Mg, Sr, Fe, Si, Al, Th and U were determined on the inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma sector field mass spectrometry (ICP-SFMS) at the ALS laboratory group in Luleå, Sweden, with measurement conditions and operation parameters described in detail elsewhere (Olofsson et al., 2000; Rodushkin et al., 2005). Water flow rates used in this study were logged hourly from automatic runoff stations close to stream outlet. Information on the installation of the stations and the measurements are given in Sjögren (2007).

A total of 18 samples of precipitation were gathered from an open field east of the catchments (Fig. 1) over a total of 18 periods from 2008 to 2012 (Supplementary information, Table S1). During each of the sampling periods, the precipitation collected with 5 samplers placed 2 to 10 m apart in an area with a diameter of approximately 25 m were emptied and mixed (Ericsson, 2008). All the precipitation samples were filtered through 0.45 μm disposable filters and analyzed for U and Th concentrations at the ALS laboratory group in Luleå, Sweden, with the same set up as above. However, pH and conductivity measurements were performed only on the samples collected between 2008 and 2009.

2.4. Geochemical modeling

The geochemical software code Visual MINTEQ version 3.1. (Gustafsson, 2014) was used to predict the metal speciation in the stream waters. Input parameters included pH, temperature, alkalinity and concentrations of major cations (Ca^{2+}, K^+, Na^+, Mg^{2+}, Sr^{2+}), anions (Cl^-, F^-, PO_4^-, SO_4^{2-}), DOC, Al, Fe, Si, Ba, U, and Th.

The redox potential (pe) is an important parameter in determining the redox speciation of Fe and U. Although the redox potential was not measured for the stream waters, in O_2-saturated waters a reasonable pe value can be estimated using the following formula: $pe = 20.78 + 1/4 \log P_{O2}$-pH (Stumm and Morgan, 1996; Wällstedt et al., 2010; Köhler et al., 2014) and assuming an oxygen pressure of 0.2 atm. Given the fact that the redox reaction for O_2 is slow and the pe-values of natural waters are often lower than the theoretical values (Langmuir, 1997), the calculated pe values should be considered as maximum values. For modeling the redox speciation of Fe and U, the redox couples Fe^{2+}/Fe^{3+} and $U^{(IV)}/UO_2^{2+}$ were added.

The NICA-Donnan model implemented in Visual MINTEQ was used to simulate the formation of metal-DOM complexes. Based on a previous study (Sjöstedt et al., 2010), it was assumed that the ratio of active DOM to DOC was 1.65 and that 82.5% of the active DOM was fulvic acid (FA) and the remaining 16.5% inactive with respect to proton and metal binding.

In the calculations, the Al, Fe and Ca in the filtered (< 0.45 μm) water samples were allowed to precipitate when the solubility products for Al $(OH)_3$ (soil) ($\log^*Ks = 8.29$ at 25 °C), ferrihydrite (aged) ($\log^*Ks = 2.69$ at 25 °C) and calcite ($\log^*Ks = -8.48$ at 25 °C) were exceeded. The log*Ks value for calcite is negative, because of the fact the equilibrium constant (Ks) for calcite at 25 °C, i.e. the product of the activities of dissolved Ca and carbonate, is equal to $10^{-8.48}$. The rationale for including these possible solid phases were: (i) previous X-ray absorption spectroscopy studies have shown that ferrihydrite- and gibbsite-like

phases dominate the total Fe and Al fractions in boreal surface waters (Sundman et al., 2014; Hagvall et al., 2015), (ii) ferrihydrite and gibbsite possess large reactive surfaces that are negatively charged under neutral and alkaline conditions, and thus have the greatest potential to act as inorganic sorbents for U and Th, and (iii) Fe, Al and Ca ions can compete with U and Th for ligand-binding sites on DOM.

Binding of U and Th to gibbsite and binding of U to ferrihydrite were modeled if these phases were predicted to occur in the water samples. Sorption of Th to ferrihydrite was not modeled, because surface complexation constants for the binding of Th to ferrihydrite are not available. Ferrihydrite and gibbsite were assumed to have a specific surface area of 600 $m^2\ g^{-1}$ and 32 $m^2\ g^{-1}$, respectively. Sorption to gibbsite and ferrihydrite was simulated with the diffuse layer model (DLM) (Karamalidis and Dzombak, 2010) and the CD-MUSIC model parameterized for ferrihydrite (Tiberg et al., 2013), respectively.

2.5. Existing data of U in aquatic samples

The concentrations and color-map of U in aquatic samples from streams in the study area were retrieved from the biogeochemistry map database (https://www.sgu.se/en/products/maps/) owned by the Geological Survey of Sweden (SGU). The database comprises of nearly 40,000 aquatic samples, consisting mainly of roots of sedge (Carex species) and meadowsweet (*Filipendula ulmaria*), and whole-plant of the bryophyte water moss (*Fontinalis antipyretica*). The aquatic plants collected within 50–100 m sections of selected streams/ditches were mixed as composite samples. About one-third of the samples included only one species, while the rest of the samples were mixed species. All samples were incinerated, and the resulting ashes were analyzed for U concentrations by X-ray fluorescence. The detailed sampling and analytical procedures are reported in Andersson et al. (2014).

2.6. Statistical analysis

Bivariate correlation analysis was used to evaluate the strength and significance of the dependence between two variables. The normality of distribution of all tested variables was checked by the Shapiro-Wilk test. For normally distributed variables, Pearson correlation was used for bivariate correlation analysis, otherwise the non-parametric Spearman method was applied. All statistical analyses and calculations were performed using IBM SPSS Statistics 24 software.

3. Results

3.1. Quaternary deposits

3.1.1. <2 mm samples (Kärrsvik stream catchment)

Total U and Th concentrations ranged from 1.3 mg kg^{-1} to 35 mg kg^{-1} and from 3.8 mg kg^{-1} to 55 mg kg^{-1}, respectively, and varied in a similar manner across individual profiles with no systematic depth-related trend (Fig. 2). Uranium was strongly accumulated in the peat/gyttja samples (Figs. 2, 3a; Supplementary information, Fig. S1),

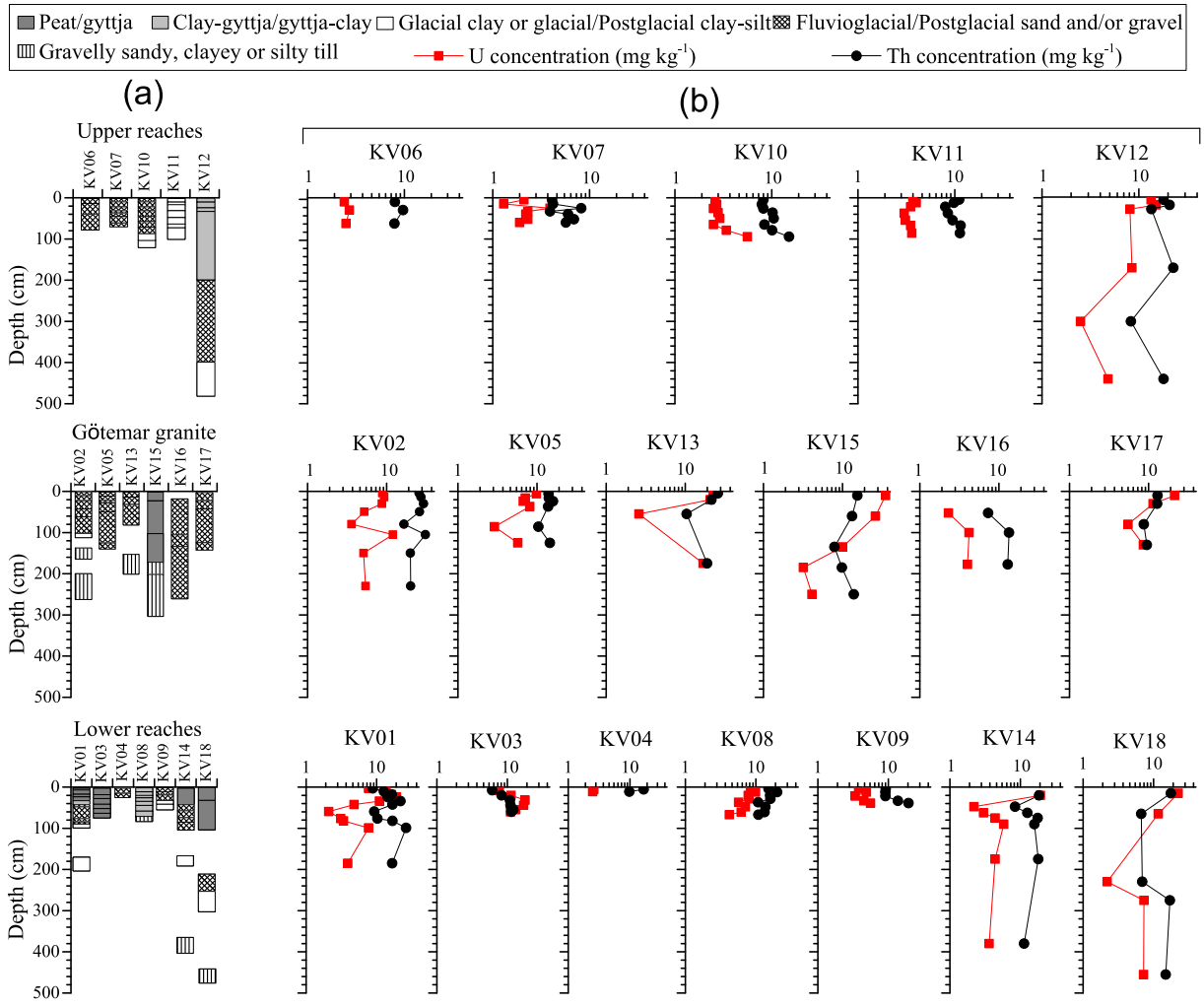

Fig. 2. Vertical distribution of different soil types (a), and U and Th concentrations (b) of Quaternary deposits from three subareas of the Kärrsvik stream catchment: upper reaches (upper row), upon the Götemar granite (middle row) and lower reaches (lower row).

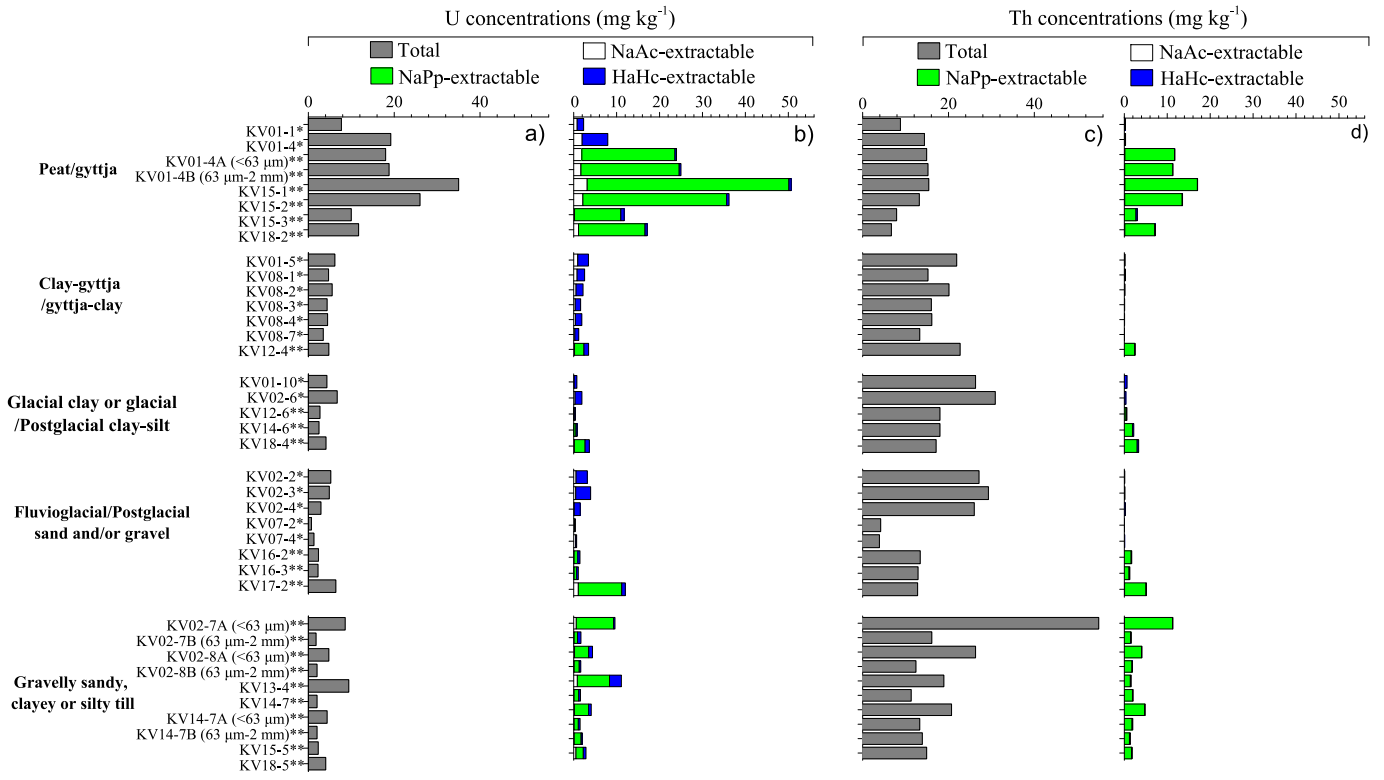

Fig. 3. Concentrations of total U and Th as well as the concentrations of U and Th extracted with Na acetate (NaAc), Na pyrophosphate (NaPp) and hydroxylamine hydrochloride (HaHc) for subsamples of Quaternary deposits grouped by soil types. The samples extracted sequentially with NaAc and HaHc were marked by *, while those extracted sequentially with NaAc, NaPp and HaHc by **. The analyses of total concentrations and sequential extractions were performed on two separate subsamples, which may at least partly explain as to why for some samples the sum of U concentration in the sequentially extracted fractions was higher than the measured total concentration.

and displayed a significant positive relationship with the values of LOI (an indicator of organic matter content) across all samples ($r_{Spearman} = 0.62$, $p < 0.01$, $n = 106$). In contrast, Th concentrations were neither elevated in the peat/gyttja samples (Figs. 2, 3c; Supplementary information, Fig. S1), nor significantly correlated with the LOI values ($r_{Spearman} = 0.05$, $p = 0.58$, n = 106). The concentrations of Th and U in samples from the lower reaches and upon the granite pluton were higher than those from the upper reaches (Fig. 4a; Supplementary information, Fig. S1).

Of the three chemical reagents used in the SCE experiment, NaPp released by far the greatest amount of U and Th (Fig. 3b, d). In particular, in the peat/gyttja samples and one sample with high LOI values (KV17–2, LOI = 11.4%; Supplementary information, Fig. S1), the U was nearly quantitatively extracted by NaPp (Fig. 3b). An exception is subsample KV13–4 where large proportions of U were extracted with NaPp, together with NaAc and HaHc, in spite of its low LOI value (0.72%; Supplementary information, Fig. S1). A majority of Th in the peat/gyttja samples were extracted by NaPp. For the rest of the samples, NaPp only released small proportions (10th–90th percentiles = 7.4%–17.5%, $n = 11$) of the total Th. In the samples for which the NaPp leach was not included, abundant U but consistently low amounts of Th were released by HaHc. Moreover, the peat/gyttja samples contained small but significantly higher quantities of NaAc-extractable U (10th–90th percentiles = 0.05–0.14 mg kg^{-1}, $n = 6$) as compared to the rest of the samples (10th–90th percentiles = 0.005–0.067 mg kg^{-1}, $n = 24$).

3.1.2. Fine and coarse fractions (Kärrsvik stream catchment)

The two size fractions (2 mm–63 μm and <63 μm) obtained from one sample of peat/gyttja (KV01-4) were almost identical in terms of LOI values (30.1% and 29.3%, respectively; Supplementary information, Fig. S1), total concentrations of U and Th, as well as size of the NaAc- and NaPp-extractable U and Th fractions (Fig. 3). In contrast, the fine fraction obtained from the other three samples (classified as gravelly sandy, clayey or silty till) contained significantly higher values of LOI (Supplementary information, Fig. S1), and higher concentrations of total and NaPp- extractable U and Th, as compared to the corresponding coarse fraction (Fig. 3).

3.2. Stream waters

The pH was slightly alkaline in the Ekerum stream (7.1–7.9) and weakly acidic in the other three streams (Kärrsvik = 5.9–6.7; Kårevik = 6.1–6.5; Laxemar = 5.9–7.0) (Fig. 5). In all the streams, the pH co-varied closely with alkalinity, but inversely with stream water flow which displayed a substantial seasonal and inter-annual variation (Fig. 5). The concentrations of DOC in all four streams were high, which is a typical feature for the streams in northern Europe (Sweden and Finland) as compared to the streams in most other parts of Europe (Fig. 6a), and displayed a similar magnitude of temporal variability in all streams (Kärrsvik = 12.7–24.1 mg L^{-1}; Kårevik = 10.1–17.9 mg L^{-1}; Ekerum = 14.3–23.6 mg L^{-1}; Laxemar = 13.2–27.5 mg L^{-1}).

Dissolved U was highest in the Ekerum stream (Fig. 4b), with concentrations ranging from 0.36 to 2.56 μg L^{-1} (Table 1), and modeled to be largely associated with DOM and also occur as $Ca_2UO_2(CO_3)_3$ (aq) and a group of negatively-charged carbonate phases ($CaUO_2(CO_3)_3^{2-}$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$), along with minor surface complexes on ferrihydrite (Fig. 5). For the other streams, the concentrations of U were considerably lower and overall decreased in the order of: Kärrsvik stream (average U concentration = 0.80 μg L^{-1}) > Kårevik stream (average U concentration = 0.56 μg L^{-1}) > Laxemar stream (average U concentration = 0.31 μg L^{-1}) (Fig. 4b), in a manner similar to the F concentrations (Fig. 5). In these streams, the dissolved U was largely bound to DOM, with very minor contributions of the carbonate phases and surface complexes on ferrihydrite (Fig. 5). Concentrations

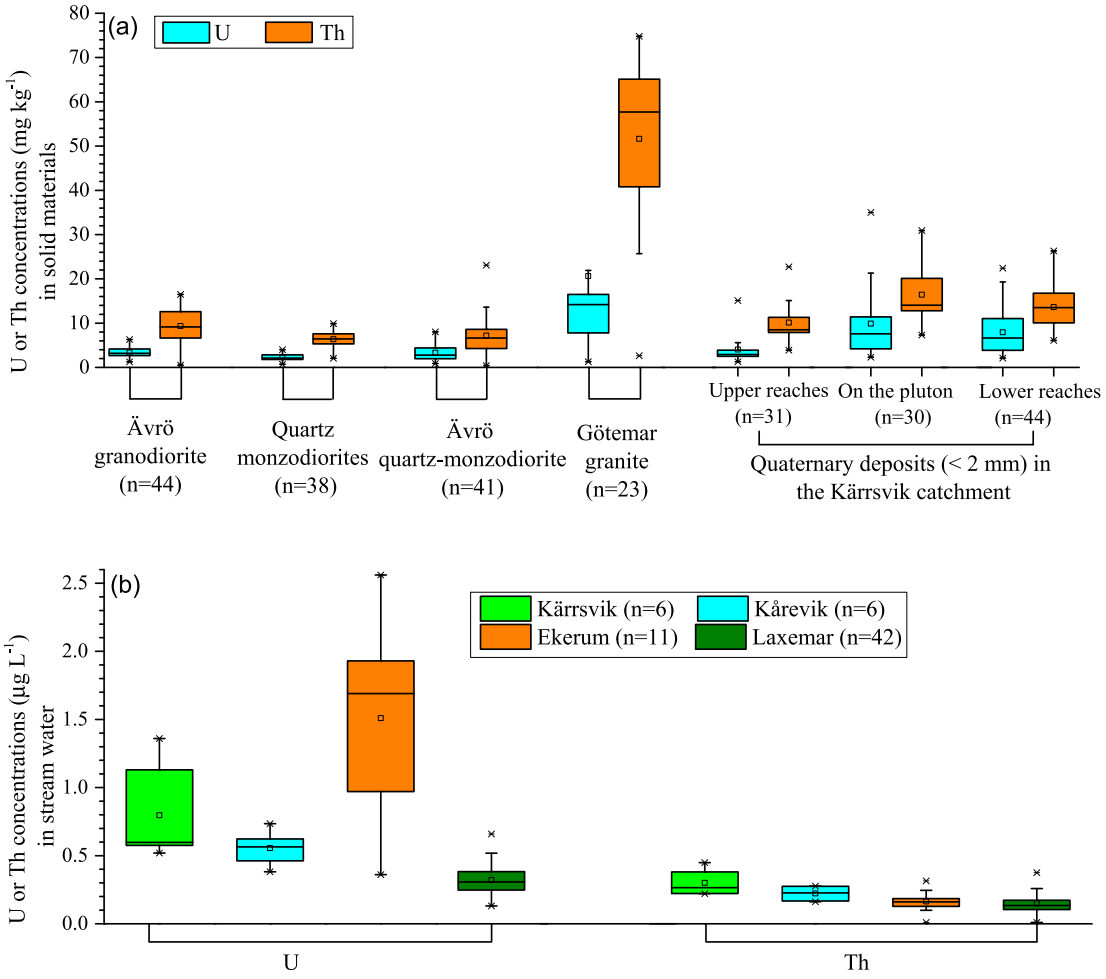

Fig. 4. Box plots of U and Th concentrations in different solid materials (a) and water samples (b) from the study area. The data for the dominant rock types and the Götemar granite were compiled from Åhäll (2001), Alm et al. (2005), Drake et al. (2008) and Drake and Tullborg (2009).

of dissolved Th displayed a continuous decrease in the order of: Kärrsvik stream (average Th concentration = 0.29 μg L^{-1}) > Kårevik stream (average Th concentration = 0.21 μg L^{-1}) > Ekerum stream (average Th concentration = 0.16 μg L^{-1}) > Laxemar stream (average Th concentration = 0.14 μg L^{-1}) (Fig. 4b). In all stream waters, Th was predicted to be entirely bound to DOM (Fig. 5). Although most of the stream waters carried abundant gibbsite colloids according to the geochemical model, no U and Th was modeled as adsorbed to this phase (Fig. 5).

3.3. Precipitation

The precipitation samples (collected between 2008 and 2011) were moderately to weakly acidic, with pH values varying by 2 units (4.5–6.5), and had consistently low conductivity (0.6–4.7 mS m^{-1}) (Supplementary information, Table S1). The concentrations of dissolved U were very low (≤ 0.0058 μg L^{-1}) in all the samples, except one outlier in March 2011 when the U concentration reached up to 0.38 μg L^{-1}. The concentrations of Th were below the detection limit of 0.0005 μg L^{-1} in all samples.

3.4. Aquatic plants

The concentrations of U in aquatic plants (roots and mosses) from the study area varied significantly (by two orders of magnitude) from <4 ppm to 365 ppm (Fig. 1). The values were highest in the central part of the granite pluton, and overall decreased with increasing distance from the pluton.

4. Discussion

4.1. Distribution of U and Th in Quaternary deposits

Total concentrations of Th and U in all samples of Quaternary deposits were significantly correlated ($r_{Spearman}$ = 0.60, $p < 0.01$, n = 113), suggesting that the distribution of these two actinides in these deposits (regolith) is governed by similar processes/phases. The results of the SCE experiment showed that large fractions of U and Th, in particular in the peat/gyttia samples, were extracted by NaPp (Fig. 3), and were thus associated with labile organic material targeted by this leach. For the peat/gyttia samples (e.g., KV15-3, KV03-5 and KV03-6; Fig. 2a) located at deep depths where oxygen supply is limited, U might be reduced either enzymatically by a broad diversity of microorganisms or chemically by reducing compounds (Ray et al., 2011; Bargar et al., 2013; Hyun et al., 2014). Apart from being precipitated as crystalline U(IV) phases (e.g., uraninite), the produced U(IV) can be largely adsorbed onto organic material via monomeric complexes as found recently for organic-rich environments elsewhere (Mikutta et al., 2016; Bone et al., 2017). These organically-complexed U(IV) phases, if present in the peat/gyttia samples, are expected to be also largely extracted during the NaPp leach. The close association between organic matter and these two actinides was further supported by the significant positive

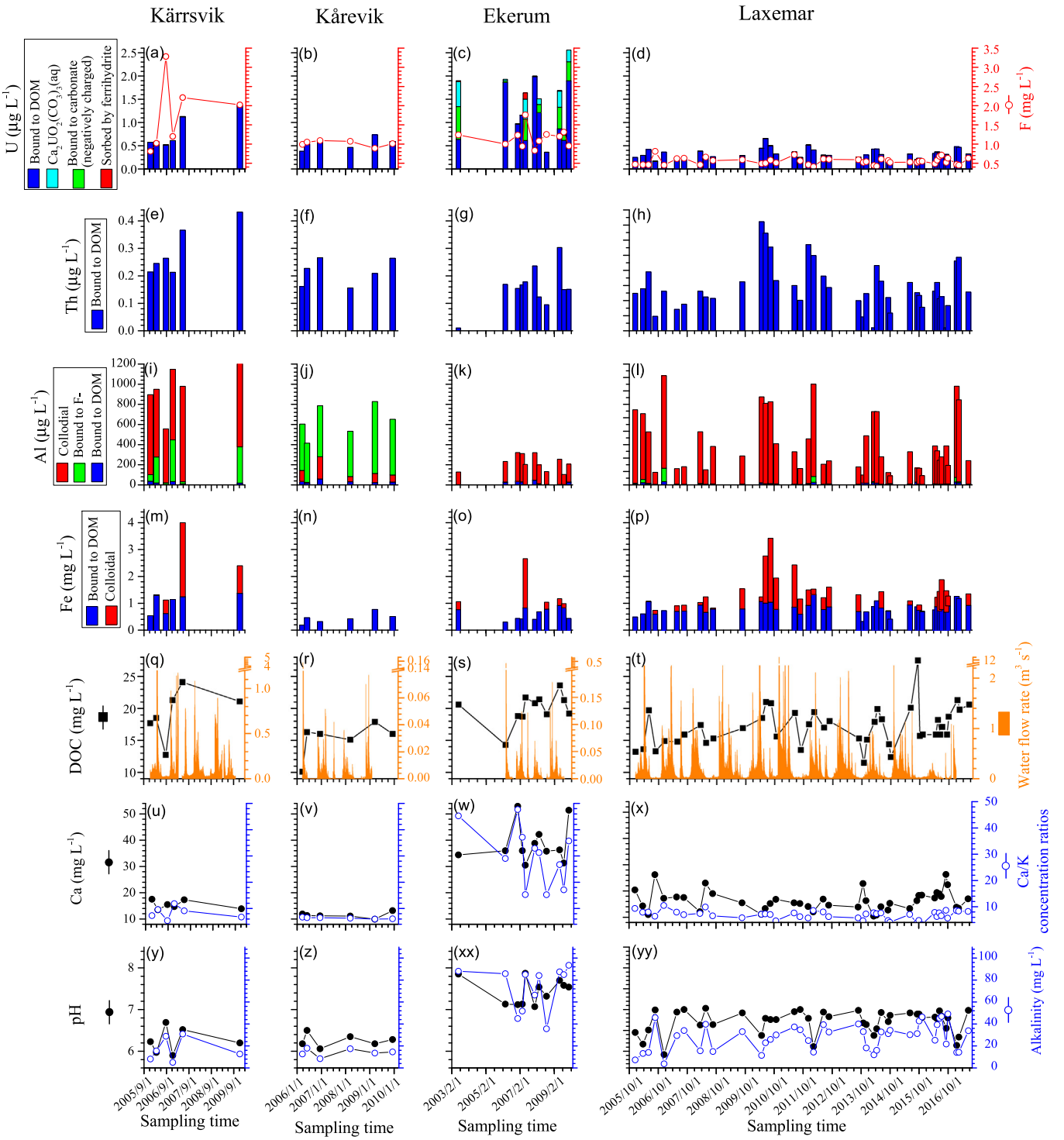

Fig. 5. Temporal variation of measured concentrations and proportion of modeled species of Fe, Al, U and Th, in comparison with other hydro-chemical variables (pH, alkalinity, water flow rate, concentrations of F, DOC and Ca, and concentration ratios of Ca/K), in the Kärrsvik stream (column to the left), Kårevik stream (second column), Ekerum stream (third column) and Laxemar stream (column to the right).

correlations between the values of LOI and the NaPp-extractable concentrations of U ($r_{Spearman} = 0.76$, $p < 0.01$, $n = 23$) and Th ($r_{Spearman} = 0.81$, $p < 0.01$, n = 23). In addition to organic material, the residual fraction remaining after the three SCE steps was a major phase for these two actinides, in particular Th (Fig. 3). In soil profiles developed in a similar granitic setting elsewhere (Spain), SEM-EDS analyses indicated that U and Th in the residual fraction are mainly associated with several common accessory minerals, such as Zr silicates (zircon and armstrongite) and phosphates (apatite, monazite, and xenotime) (Taboada et al., 2006).

Another feature for the Quaternary deposits was that NaAc, targeting water soluble, exchangeable and carbonate-bound phases, extracted much larger quantities of U than Th and considerably larger quantities of U from the peat/gyttja than from the other soil types (Fig. 3). The peat/gyttja samples were weakly acidic (pH = 4.5–6.0) (Berger et al., 2016), and therefore did not provide favorable conditions for the

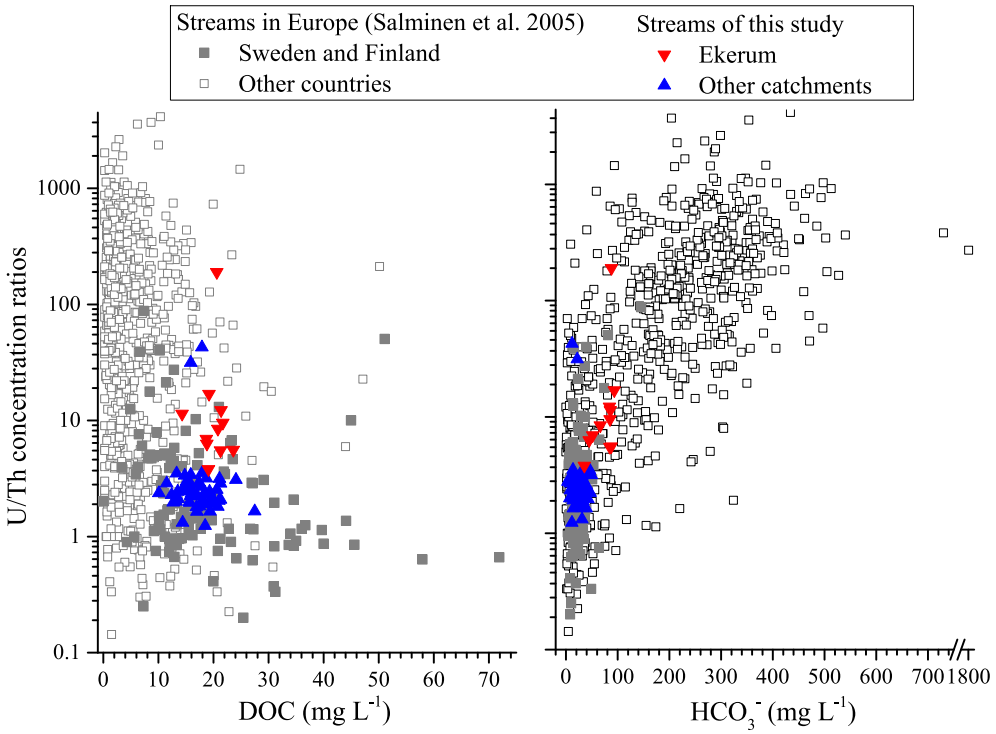

Fig. 6. The ratios of U concentrations to Th concentrations as a function of the concentrations of DOC and HCO_3^- for the streams of this study and throughout Europe (Salminen et al., 2005). The European streams were divided into those in Sweden + Finland (representing northerly areas with a large share of forests and mires) and all the other countries on the continent.

formation and preservation of carbonate minerals, which strongly reduces the likeliness of carbonate as a main phase for NaAc-extractable U. Instead, the concentrations of NaAc-extractable U were strongly correlated with the values of LOI ($r_{Spearman} = 0.79$, $p < 0.01$, $n = 38$), suggesting that the U extracted by this step mainly represented exchangeable U complexed with organic matter. The partial release of organically complexed U by NaAc before the application of the NaPp is also consistent with experiments showing that, under acidic conditions, the release of U could occur without dissolution of organic matter (Regenspurg et al., 2010). In contrast, extractability of Th by NaAc was limited that might be due to the fact that Th has an even stronger affinity for organic matter (Lidman et al., 2012), and thus can bind to organic matter more tightly than U.

4.2. Impact of atmospheric deposition and agrichemical activities

Precipitation samples from the study area contained higher levels of U than Th that was undetectable during all sampling periods (Supplementary information, Table S1). Although the study area is located close to the Baltic Sea, the contribution of seawater spray was overall minimal, as reflected by the low concentrations of chloride (0.3–2.7 mg L^{-1}) in the precipitation samples (Supplementary information, Table S1). Based on the median concentrations of U and Th in the precipitation samples (assumed to be half of the reported detection limit for Th) and annual average precipitation in the study area (600 mm), the annual atmospheric deposition of U and Th was estimated to be 1.38 mg km^{-2} and 0.15 mg km^{-2}, respectively, accounting for <3.5% of the annual fluxes of Th and U exported from the four catchments (Table 1).

It has been shown that intensive application of chemical fertilizers can significantly elevate U concentrations in cultivated soils (Ahmed et al., 2014). Although farmland occurs more abundantly in the Ekerum catchment where the dissolved U concentrations were by far the highest (Figs. 4b, 5; Table 1), agrichemical activities (e.g., the application of P- and N-rich fertilizers) are highly unlikely to be responsible for the elevated U concentrations in this stream because (i) the concentrations of P and NO_3^- were as low as in the other streams (Table 1); (ii) the concentrations of U were not significantly correlated with those of NO_3^- ($r_{Spearman} = 0.34$, $p = 0.31$, $n = 11$), a highly soluble species that has been used to trace the drainage from irrigated and fertilized soils (Zielinski et al., 1997). The result is consistent with previous studies showing that the application of fertilizers has minimal impact on riverine loads of U (Zielinski et al., 1995, 1997, 2006), unless the watercourses receive very low natural input of U (Zielinski et al., 2000; Conceição and Bonotto, 2003). Taken together, atmospheric deposition and agrichemical activities have a very minor influence on the total fluxes of U and Th in the study area. Hence, the total fluxes of U and Th are mainly lithogenic and derived from the weathering of Quaternary deposits and exposed bedrock.

4.3. Impact of the U- and Th-rich granite

It is evident that the Götemar granite pluton is strongly enriched in both U and Th, relative to the dominant rock types in the area (Fig. 4a). Although the pluton is in direct contact only with a small part of the Kärrsvik catchment, the movement of the ice sheet during the latest glaciation has eroded the surface of the pluton and transported the erosional materials (e.g., mineral particles and rock fragments) southward and southeasterly (Berger et al., 2012). These processes should have resulted in a large spreading of U- and Th- rich materials towards the southern and southeastern sides of the pluton, covering the lower reaches of Kärrsvik and Laxemar streams and the entire catchments of Kårevik and Ekerum streams. Indeed, the Quaternary deposits in the lower reaches of the Kärrsvik stream, located to the southern side of the pluton, contained higher levels of U and Th than the deposits in the upper reaches of the stream with no or very limited input of erosional materials from the pluton (Fig. 4a). These U- and Th-rich materials resided mainly within till and glaciofluvial clay and/or silt deposited in the low-lying areas where the streams flow. In line with these features and processes, the concentrations of U and Th displayed an overall decreasing trend in stream water with increasing distance from the granite (Fig. 4b), in a manner similar to the F concentrations

that have been found to be controlled by weathering of the Götemar granite and its erosional materials (Berger et al., 2012). The only exception was the U concentrations in the Ekerum stream that was controlled by other mechanisms as described below. The occurrence of the granite pluton also has exerted a strong impact on the adjacent aquatic ecosystems, as reflected by the fact that the concentrations of U in plant roots or aquatic mosses in streams were highest in the central part of the pluton and decreased away from the pluton (Fig. 1). Taken together, these features show that the granite pluton and its erosional products residing in the soils have a profound effect on the U and Th concentrations and bioavailability in stream water.

4.4. Factors affecting transport and fractionation of U and Th in forested boreal landscapes

When U/Th concentration ratios in the studied streams and in streams throughout Europe are plotted as a function of the concentrations of DOC and HCO_3^- (Fig. 6), it is seen that the streams from our study area overlap with streams draining extensive forest and mire areas in northern Europe (Sweden and Finland) in terms of DOC concentrations (high), alkalinity (low), and U/Th ratios (consistently low despite that the concentrations of DOC varied by three orders of magnitudes). These features indicate that the transport and fractionation of U and Th in our study area, despite the occurrence of an U- and Th rich granite and its substantial effect on the dispersion of U and Th, are similar to those in other forested catchments in northern Europe, and thus, are governed by fundamental geochemical processes.

Peat and mire have been demonstrated to be effective adsorbents for U in both artificial and natural water systems at environmentally relevant U concentrations, with enrichment factors (the ratio of the U concentration in dry peat and mire samples to that in coexisting water) reaching up to 0.9×10^4–2×10^6 (Kochenov et al., 1965; Armands, 1967; Szalay, 1969; Porcelli et al., 1997; Schumann et al., 2017). Assuming the water infiltrating the peat/gyttja (sampled in the Kärrsvik stream catchment located close to and partly upon the Götemar granite) had an average U concentration of 0.80 μg L^{-1} (the average concentration in the water at the outlet of this stream), the peat/gyttja samples from the catchment concentrated U by a factor of $2.5 \times 10^4 \pm 9 \times 10^3$ that is within the values reported by previous laboratory and field experiments. Although no data are available regarding the adsorption of Th by peat, mire or other similar organic materials, the peat/gyttja samples were enriched in Th by a factor of $4.2 \times 10^4 \pm 1.3 \times 10^3$ relative to the stream water. This value is approximately two times higher than the corresponding value for U, in line with the fact that Th in the Quaternary deposits was released almost exclusively with NaPp and to only a very minor extent with NaAc and HaHc (Fig. 3). These features suggest that after being released from the outcropping U- and Th-rich Götemar granite (and other exposed bedrock) and mineral soils, these two actinides (in particular Th) were efficiently trapped by the peat/gyttja and redistributed from the inorganic to the organic fractions in other Quaternary deposits. A part of the released and probably a part of the soil-organically complexed U and Th became bound to soluble organic matter that transported these metals downstream, as evidenced by the fact that the dissolved pools of these actinides were (i) modeled to be nearly quantitatively bound to DOC; and (ii) positively correlated with the concentrations of DOC, except for U in the Ekerum stream (Fig. 7a, b), where the U mobilization and transport were enhanced greatly by specific hydro-chemical conditions as discussed below.

Lidman et al. (2012) investigated geochemical processes controlling the transport of U and Th in 10 forested sub-catchments within the Krycklan catchment in northern Sweden. Although their Minteq modeling predicted that >96% of the U and an even higher proportion of the Th is complexed with DOC, the annual fluxes of U and Th were inversely correlated with those of DOC. The authors attributed this feature to the fact that wetlands, occurring abundantly (14–50%) in 6 of the 10 sub-catchments, are the main source of DOC to the streams, but act as

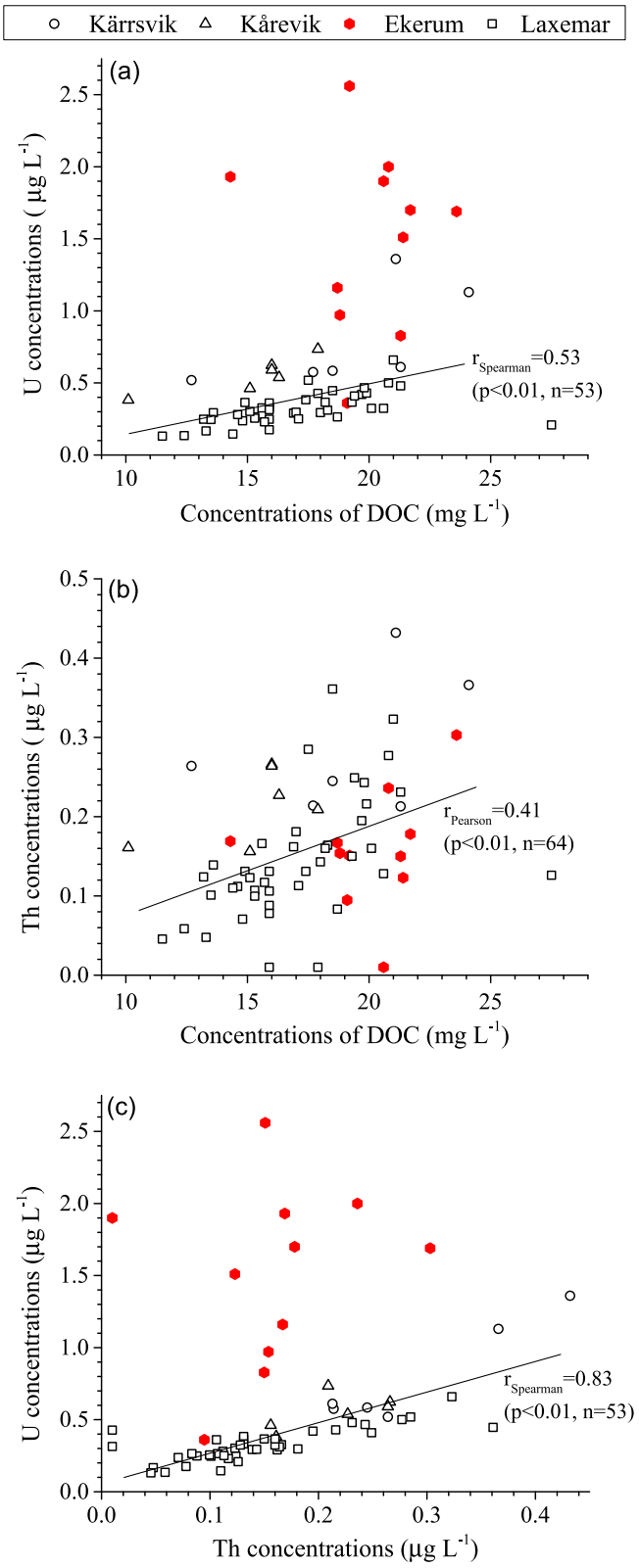

Fig. 7. The concentrations of DOC versus those of U (a) and Th (b), and concentrations of U versus those of Th (c) for water samples from the four streams. The correlation coefficients in (a) and (c) were calculated based on the water samples from the Kärrsvik, Kårevik and Laxemar streams, while the one in (b) was based on all the water samples.

an efficient sink for U and Th. As such, 4 of the 10 streams running through forested landscapes with lower coverage of wetland (1.3–8.6%) carried highest fluxes of U (16–30 g km^{-2} a^{-1}) and Th

(16–24 g km^{-2} a^{-1}), because of their high dissolved concentrations of U (between 0.04 and 0.19 μg L^{-1}) and Th (between 0.04 and 0.15 μg L^{-1}). As compared to these four streams within the Krycklan catchment, the streams in our study area were similar in terms of catchment features (i.e. 84–88% of the total catchment area is covered by coniferous forests), and concentrations and annual export of Th, but had much higher concentrations and fluxes of U (Table 1). The latter feature is attributed to a combination of two processes. First, oxidizing condition in the surface environment strongly favors the leaching and mobilization of U enriched in the granite pluton and Quaternary deposits as compared to Th that is frequently considered as an immobile reference element for assessing the mobility of other elements (Braun et al., 1993; Ma et al., 2007). Second, released Th is trapped by organic matter more effectively than U, due to the very strong association between Th and organic matter in the Quaternary deposits as revealed by our SCE data (Fig. 3).

It has been shown that the presence of uncharged $Ca_2UO_2(CO_3)_3^0$ (aq), a highly stable and soluble U species that commonly occurs in circumneutral and alkaline environments (Prat et al., 2009; Tullborg et al., 2017), can significantly enhance the mobility of U by decreasing its sorption efficiency (Fox et al., 2006; Nair and Merkel, 2011). The formation of this non-absorbing species may have a strong impact on the mobilization of U on a continental scale, as evidenced by significant correlations between the concentrations of U and those of HCO_3^- and Ca in geochemical atlases covering 808 streams throughout Europe and 685 streams in the Phanerozoic area in western Russia (Åström et al., 2009). This species was predicted to occur in relatively large proportions in the Ekerum stream, where circumneutral and alkaline conditions prevailed (Fig. 4), and the U concentrations (and therefore also the ratios of U to Th) were considerably higher than in the other streams (Figs. 4b, 5a–d, 7c). In contrast to the other streams, the Ekerum stream is characterized by not only high pH and alkalinity, but also strongly elevated concentrations of Ca and high ratios of Ca/K (Fig. 5u–x), suggesting a strong input of Ca from non-silicate phases, most probably calcite, in the catchment. It is thus suggested that the formation of uranyl-Ca-carbonate complexes under circumneutral/alkaline conditions within the Ekerum stream catchment enhanced the release and subsequent transport U from Quaternary deposits, in particular erosional materials derived from the Götemar granite.

Due to the effects of future global climate change, catchments in northern Europe will experience higher air temperatures and more frequent and longer periods of droughts followed by heavy precipitation (Andréasson et al., 2004; Graham, 2004). There are thus reasons to believe that the partially degraded organic matter preserved in these catchments will be decomposed and oxidized more rapidly and to a greater extent than at present, causing an increase in the amount of soluble and water-dispersible organics as well as alkalinity (Fenner and Freeman, 2011). The soluble and water-dispersible organic compounds can cause an increase in the dispersion and transport of both Th and U, while the alkalinity is likely to favor the formation of uranyl-Ca-carbonate complexes that further increase U dispersion. As such, the U (and Th) released by the Götemar granite will be trapped to a lesser extent by the diminishing pool of organic matter. Climate change is thus a key parameter in assessing and predicting future mobilization, transport and environmental effects of U and Th in these northerly landscapes.

5. Conclusions

The weathering of a large U- and Th-rich granite pluton and glacial debris (till and glaciofluvial clay and/or silt) derived from it has enhanced the dispersion and transport of both U and Th into the neighboring aquatic environment. These processes are more prominent for U, and thus significantly increased the stream flux of U beyond values typically encountered for boreal streams. Large proportions of U and Th pools in the Quaternary deposits, in particular in peat/gyttja, were extracted by Na pyrophosphate and thus associated largely with organic matter. This indicates that, after being released from primary minerals in bedrock and soils, both U and Th have been largely scavenged by organic material composing peat/gyttja and contained within other Quaternary deposits.

Geochemical calculations and correlation analyses suggested that dissolved organic matter acts as an important vehicle for the transportation of U and Th in the streams, and that the formation of uncharged uranyl-Ca-carbonate complexes under slightly alkaline conditions further enhances the release and subsequent export of U. Future change in hydrochemical conditions in boreal catchments, such as more frequent warmer and drier periods followed by intensified precipitation as a result of climate change, may increase the availability of soluble dissolved organic matter and alkalinity favoring further release and export of U and Th.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.01.293.

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